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⑳ Cookware.

㉑ Cookware having a non-stick cooking surface is formed by roughening an aluminium surface, hard anodizing that surface to give a hard anodized layer of 15 to 50 microns in thickness, and finally adhering a non-stick coating, eg. of PTFE, to that surface, optionally with a primer layer between the hard anodized surface and the non-stick coating.

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## COOKWARE

This invention relates to cookware having a non-stick cooking surface. Also the invention relates to the application of a non-stick coating such as polytetrafluoroethylene (PTFE) to an aluminium substrate which can thereafter be used for cookware.

It is very well known to apply various non-stick surfaces to cookware and by far and away the most widely used and best known non-stick surface is that provided by a PTFE coating. Such coatings are applied to the interior surfaces of cookware and the cookware may for example be made from a number of materials including aluminium.

There are however problems in the abrasion resistance of such a PTFE coating since it is a relatively soft material and so easily scratched. However problems of scratching are made much worse when the cookware is made of aluminium rather than say stainless steel. Thus, aluminium is relatively a soft material and can itself be scratched very easily by metal cooking utensils or simply by rough usage of nylon and wooden spatulas. Deep scratches can therefore be cut into the aluminium and the spreading of the aluminium when it is scratched tends to make the scratch much wider than one would expect and thereafter the PTFE coating will quickly peel away from the scratch to give a large bare area.

Non-stick PTFE coatings are therefore more scratch and abrasion resistant when they are applied to harder substrates such as porcelain frit coated aluminium, stainless steel or aluminium oxide coated aluminium.

German Patent Specification No. 1 546 934 describes the coating of an aluminium surface which has been anodized with a non-stick coating. The aluminium surface is first etched and then anodized. However, during anodizing the sharpness of the roughening of the surface is lost since anodizing tends to dissolve away the sharp points of the roughening. Therefore the bonding of the non-stick coating to be anodized layer is not satisfactory even though the anodizing does harden the surface.

Therefore it is an object of the invention to provide an improved, durable and scratch resistant surface where the non-stick coating is applied to an aluminium substrate since aluminium cookware has substantial advantages in view of its high heat conductivity and relatively light weight.

According to the invention there is provided a method of making aluminium cookware having a non-stick food-contacting surface, in which an aluminium substrate is roughened and then anodized at least in the region of its intended food-contacting surface, and a non-stick coating is applied to and adhered directly to that anodized surface, characterised in that the anodizing is hard anodizing and that a hard anodized layer of 15 to 50 microns in thickness is formed.

The invention also extends to the aluminium cookware made by this method.

Further according to another aspect of the invention there is provided a piece of aluminium cookware having a non-stick food-contacting surface, that surface comprising a non-stick coating adhered directly to a roughened porous anodized surface of the cookware, characterised in that the anodizing is hard anodizing and the anodized layer is 15 to 50 microns in thickness.

In this way the non-stick coating becomes very tightly bonded to the aluminium surface as will be described and in addition the aluminium surface itself is made very hard by the hard anodizing process.

By far and away the best non-stick material known at the moment for non-stick cooking surfaces is PTFE. This is a well known material and is supplied under the mark Teflon by Du Pont Company in America. The invention is, however, applicable to other non-sticking coating materials and examples are silicone polymers and polyether sulphone.

The anodizing of the aluminium surface is hard anodizing since, although that is more expensive than simple anodizing, the resulting hard anodized surface is very much harder than a normal anodized surface.

The anodizing and hard anodizing of an aluminium surface are well-known techniques and involve using the aluminium substrate as an anode in an electrolytic bath so that the aluminium surface becomes exposed to and reacts with the very active oxygen which is released at the anode. Usually the electrolyte comprises a strong acid such as sulphuric acid to secure good conduction and the ability to continue operation otherwise the anodized layer may act as an electrical insulator. Typically the anodized layer which is formed during normal anodizing is 7 to 10 microns in thickness. Much thicker layers, eg of 15 to 50 microns in thickness can be achieved, however, during hard anodizing by increasing the time of the treatment and keeping the temperature of the electrolyte low, and it is preferred, according to one embodiment of the invention that the anodized layer be 35 to 40, microns in thickness.

The hard anodizing process as compared with a simple anodizing process involves the use of a lower temperature, a higher current density and an increased time of treatment. It is possible also to achieve a thicker anodized layer both overall, eg. 200 microns, and in the same unit time, eg. 10 microns in 30

minutes for normal anodizing compared with 40 microns in 35 minutes for hard anodizing. Further the resulting hard anodized layer is significantly harder than a simple anodized layer in that, for example, one can achieve a maximum hardness of about 200 (on Micron Vickers Scale) for a simple anodized layer whereas for a hard anodized layer the hardness is generally from 350 to 450 on the same scale.

The following comparison can be made as between anodizing and hard anodizing as required according to the invention:

	Normal	Hard
Acid used	acetic, sulphuric, chromic	sulphuric
Concentration of acid	10-20% (sulphuric)	10-20%
Temperature of bath	room temp (20 ° C)	below 5 ° C
Amp density used	90-110 Amp/m <sup>2</sup>	280-400 Amp/m <sup>2</sup>
Time of anodizing	10-30 min	20-200 min

During normal anodizing we have found that there is an almost linear growth of thickness of the anodized layer with time up to 5 to 7 microns in thickness. Then it becomes increasingly difficult to achieve a gain in thickness for the anodized layer and 15 microns is about the maximum thickness attainable irrespective of time. The reason is that the acid attacks and dissolve the anodized layer and in particular the attack is initially and predominantly directed to the peaks and projections of the roughened layer. The roughened surface is therefore eaten away and the sharpness of the roughening lost.

By contrast we find that following the hard anodizing process, the cold bath temperature keeps the surface of the anodized layer cool and reduces the dissolving of the anodized layer, particularly if the bath is very well agitated. Therefore with hard anodizing it is possible to retain the sharp roughened surface and to achieve a thick anodized layer.

Therefore by following the invention one has the advantage of a very hard underlying surface, which as explained above reduces the chances of scratching and of any scratches from spreading, and at the same time one has excellent adherence between the rough hard anodized surface and the non-stick coating, which reduces the chance of the non-stick coating separating from the hard surface.

At the end of the hard anodizing process, the aluminium surface has become very porous. Normally before such a hard anodized surface is used in cookware as an exposed surface to be in contact with the food, it is sealed to fill up pores in the porous surface. Typical sealing agents are nickel acetate, cobalt acetate and high pressure steam.

In accordance with the invention, however, these pores are not sealed in this way and the anodized surface is deliberately left in its porous state and the primer coating and the non-stick coating are applied, or in other words the non-stick coating is applied to and adhered directly to that porous surface just as it is after the anodizing step has been completed. They are able to penetrate into this porous surface and become very firmly fixed in place. In particular smaller molecules of the non-stick material in the primer can migrate into the pores during the curing and such molecules then provide a very strong link between the porous aluminium and the resulting cured non-stick material surface so giving a stronger bond in addition to the usual mechanical bond. This greatly improves the adhesion of the non-stick coating to the aluminium surface. Also the aluminium surface, because it has been hard anodized, is about twice as hard as stainless steel and so it is not easy to scratch it and so damage the coated surface.

Our tests on the resulting surface have shown that it can be at least three times more abrasion resistant than the best non-stick PTFE surfaces on the market today.

As a first step, and before the aluminium is hard anodized, the aluminium surface to be treated should be roughened such as by the well known grit-blasting process and/or an etching process by chemical, or electro-chemical, means to produce a surface roughness within the range of 100 to 300 microinches in its profile.

The invention will now be described, by way of example, with reference to the accompanying drawings, in which:

Figure 1 is an enlarged diagrammatic section through a part of an aluminium substrate before anodizing;

Figure 2 is a diagrammatic section similar to Figure 1 after the anodizing step; and

Figure 3 is a greatly enlarged section through a piece of cookware provided with a non-stick coating according to the invention.

Referring to the drawings, an aluminium substrate such as the base of a cooking pan has a top surface 12. As best shown in Figure 1 this has first of all been grit-blasted or etched, chemically or electro-

chemically, to provide a roughened surface with a degree of roughness of, for example, 100 to 300 microinches in its profile.

Thereafter that top surface has been hard anodized to give an anodized region 14.

As can be seen this provides a very porous and open structure on the top surface 12.

- 5 No filling of this porous surface 12 is made but instead a non-stick surface 16 is applied. This comprises a primer layer 18 applied directly to this porous surface. The primer is, for example, a polyphenylene sulphide which also contains a proportion of PTFE. The primer penetrates into and fills the pores in the region 14. Over the primer layer 18 is applied a layer 20 of PTFE.

- 10 Thereafter the whole is cured in a conventional manner by heating to about 427°C, which cures the primer and the PTFE to provide the non-stick surface 16.

- Some of the PTFE molecules in the primer, particularly those of lower molecular weight, are believed to be able to migrate into the porous anodized surface, and examples are those reference 22. Although they do not adhere chemically to the aluminium they can become mechanically trapped. Also some of them will stick together with the molecules in the layer 20 so giving a very strong mechanical connection of the layer 20 to the aluminium in addition to that given by the primer layer. It is in this way that it is believed that the very strong bond found to exist between the non-stick layer comprising the primer layer 18 and PTFE layer 20 occurs.

## 20 Claims

1. A method of making aluminium cookware having a non-stick food-contacting surface, in which an aluminium substrate is roughened and then anodized at least in the region of its intended food-contacting surface, and a non-stick coating is applied to and adhered directly to that anodized surface, characterised in that the anodizing is hard anodizing and in that a hard anodized layer of 15 to 50 microns in thickness is formed.
- 25 2. A method as claimed in Claim 1 in which a hard anodized layer of 35 to 40 microns in thickness is formed.
3. A method as claimed in either preceding claim in which the non-stick coating is a PTFE coating.
- 30 4. A method as claimed in any preceding claim in which the non-stick coating comprises a primer layer containing some of the non-stick coating material and an outer layer of the non-stick material.
5. A method as claimed in any preceding claim in which the said food-contacting surface has been sand blasted.
6. A method as claimed in any of claims 1 to 4 in which the said food-contacting surface has been
- 35 roughened by chemical or electro-chemical etching.
7. A piece of aluminium cookware made by a method as claimed in any preceding claim.
8. A piece of aluminium cookware having a non-stick food-contacting surface, that surface comprising a non-stick coating adhered directly to a roughened, porous anodized surface of the cookware, characterised in that the anodizing is hard anodizing and the hard anodized layer is to 50 microns in thickness.
- 40 9. Cookware as claimed in Claim 8 in which the hard anodized layer is 35 to 40 microns in thickness.
10. Cookware as claimed in Claim 8 or Claim 9 in which the non-stick coating is a PTFE coating.
11. Cookware as claimed in any of Claims 8 to 10 in which the non-stick coating comprises a primer layer containing some of the non-stick coating material and an outer layer of the non-stick material.

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FIG. 1

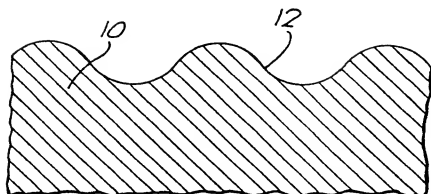


FIG. 2

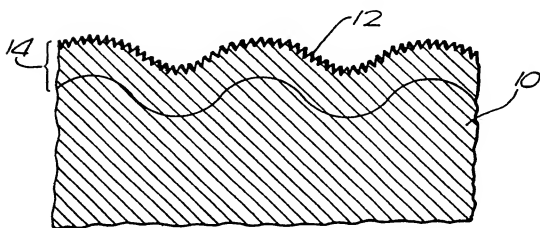
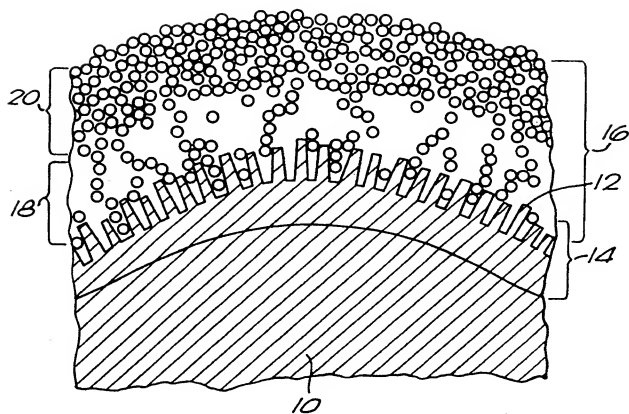


FIG. 3





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# EUROPEAN SEARCH REPORT

Application Number

EP 90 31 1275

## DOCUMENTS CONSIDERED TO BE RELEVANT

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (int. Cl.5)
Y,D	DE-A-1 546 934 (FISSLER) * The whole document * - - -	1-11	C 25 D 11/18 A 47 J 36/02
Y	S. WERNICK et al.: "The surface treatment and finishing of aluminium and its alloys", 4th edition, vol. 2, 1972, pages 566-568, Robert Draper Ltd, Teddington, GB - - -	1-11	
Y	S. WERNICK et al.: "The surface treatment and finishing of aluminium and its alloys", 5th edition, vol. 2, 1987, pages 189,1141-1143, Finishing Publications Ltd, Teddington, GB * Pages 189,1141-1143 * - - -	1-11	
A	US-A-3 574 071 (COVINO) - - - - -		
			TECHNICAL FIELDS SEARCHED (int. Cl.5)
			C 25 D 11/18
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		30 November 90	VAN LEEUWEN R.H.
CATEGORY OF CITED DOCUMENTS			
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